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Synthesis and Mesomorphic Properties of Two Series of Hydrogen-Bonded Liquid Crystals Based on Laterally Fluorinated Benzoic Acid and 4, 4'-Bipyridine With a Molar Ratio of 2:1

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Two series of hydrogen-bonded liquid crystal complexes have been obtained from binary mixtures of 4, 4'-bipyridine and 2-fluoro-6-X-4-alkoxybenzoic acids (where X = H or F) with a molar ratio of 2:1. The fluorinated proton donors were synthesized firstly and then their chemical structures measured by EA, FTIR, ¹H NMR and ¹³C NMR. The existences of hydrogen bonds between the proton donors and acceptors were identified by FTIR. The liquid crystalline properties of these complexes were investigated by differential scanning calorimeter (DSC), polarizing optical microscopy (POM), and X-ray diffraction (XRD). The results indicated that these complexes with different alkoxy chains and numbers of lateral fluorine atoms exhibited different phase properties. Especially, when the alkoxy chains were short enough, the mesophase of the complexes disappeared.

Keywords Fluorinated liquid crystal; hydrogen-bond; mesomorphic properties; synthesis

Introduction

Intermolecular hydrogen bonding has attracted much attention because it offered the possibility of incorporating diversified molecular designs [1, 2]. Novel mesogenic properties can be obtained from supramolecular architecture through hydrogen bonding between various proton donors and acceptors. In recent years, the study of thermotropic liquid crystals induced by intermolecular hydrogen bonding between different species [3–11] has attracted considerable interest since Kato and coworkers showed that hydrogen bonding between 4-alkoxybenzoic acids and pyridine derivatives was responsible for the formation or stabilization of liquid crystal phases [12].

Previous studies [13] indicate that the replacement of one or several hydrogen atoms by fluorine conferred to the resulting material unusual and peculiar properties, such as optical and chemical stability, wide mesomorphic temperature range, low melting point,

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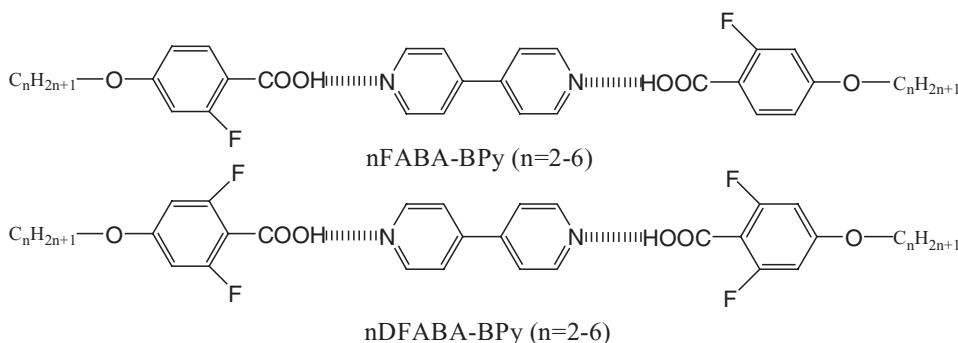


Figure 1. Aim structure of the laterally fluorinated hydrogen-bonded complexes.

low viscosity, and low conductivity. So, the studies of fluorinated liquid crystals are of great importance, and many researchers [13–15] have devoted themselves into this field. But to our knowledge, few studies [16, 17] have concerned on hydrogen-bonded liquid crystal complexes with fluorinated species.

The aim of this work was to obtain new supramolecular liquid crystals induced by intermolecular hydrogen bonding by using 4,4'-bipyridine as the proton acceptors, and 2-fluoro-6-X-4-alkoxybenzoic acids (where X = H or F) as the proton donors, whose structures were indicated in Fig. 1, and to study their mesomorphic properties by using differential scanning calorimeter (DSC), polarizing optical microscopy (POM), and X-ray diffraction (XRD).

Experiment

IR spectra were recorded on a Nicolet 510P instrument and ^1H NMR and ^{13}C NMR spectra on Bruker AV400 instrument in CDCl_3 . EA measurements were carried out on a Thermo Finnigan Flash EA1112 elemental analyzer. The mesomorphic properties of the compounds and complexes were studied by an Olympus BX-51 polarizing microscope equipped with a Linkam Scientific LTS 350 heating/freezing stage. The smectic phase was determined by their optical textures and was further confirmed by a Philip 1700 type XRD instrument. For DSC, a Perkin-Elmer DSC-6 instrument was used, the scanning rate was $10^\circ\text{C min}^{-1}$, the samples were sealed in aluminum capsules and the holder atmosphere was dry nitrogen.

The synthetic route to these complexes was shown in Fig. 2, procedures were summarized below. All reagents were commercially available. All complexes dealt with in this study were prepared similarly and the whole process for the preparation of 6FABA-BPy, 6DFABA-BPy, and their corresponding hydrogen bonded complexes were described as examples.

Synthesis of 2-Fluoro-4-Hexyloxybenzoic Acid (6FABA)

The mixture of 13.7 g (0.1 mol) 2-fluoro-4-hydroxybenzonitrile, 4.4 g (0.11 mol) NaOH, 4 g anhydrous KI, 0.11 mol hexyl bromide, and 100 mL butanone were heated to 60°C for 10 h. After cooling, the insolubles were removed and the filtrate was washed with 10%

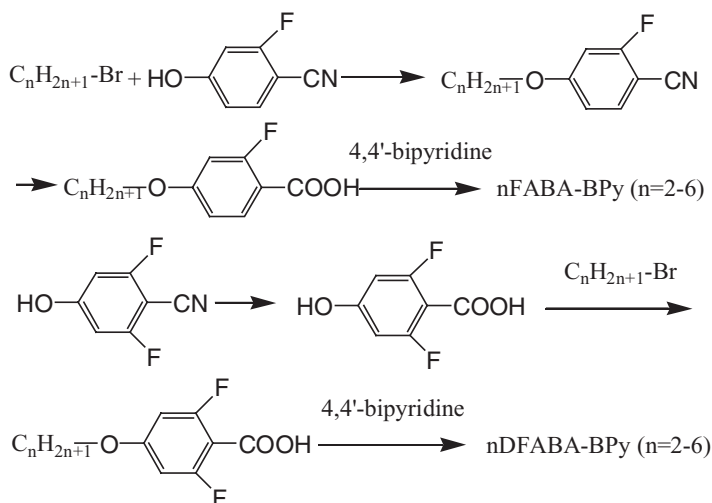


Figure 2. Synthesis route of the aim structures.

NaOH water solution for two times. The butanone was then removed through evaporation and the residues were mixed with 80 mL 10% NaOH water solution, refluxing for 24 h. After cooling, the mixture was acidified with hydrochloric acid, and the precipitate was collected by suction filtration, recrystallized from 95% ethanol. The yield was 72%, m.p. 108.2°C–112.1°C. FTIR, ν cm^{-1} : 2552–3170 (acidic —OH stretching), 1684 (C=O stretching), 1575, 1508 (aromatic C=C stretching), 1242 (C—O stretching). ^1H NMR (400 MHz, CDCl_3): δ 0.92–1.86 (m, 11H, alkyl protons), δ 4.01–4.04 (d, 2H, $\text{—CH}_2\text{—O}$), δ 6.65–6.76 (d, 2H, Ar—H), δ 7.96–8.01 (m, 1H, Ar—H). ^{13}C NMR (100 MHz, CDCl_3): δ 14.13, 22.69, 25.70, 29.00, 31.61, 68.93, 102.76 (d, $^2J_{\text{CF}} = 25.4$ Hz), 109.54, 110.90, 134.16, 165.17, 165.71 (d, $^1J_{\text{CF}} = -260.02$ Hz), 169.74. Elemental analysis: calculated (found) for $\text{C}_{13}\text{H}_{17}\text{FO}_3$ C 64.98 (65.06), H 7.13 (7.10).

Synthesis of 2, 6-Difluoro-4-Hexyloxybenzoic Acid (6DFABA)

2, 6-difluoro-4-hydroxybenzonitrile 15.5 g (0.1 mol) was added to 100 mL of 10% NaOH water solution, refluxing for 24 h, and then acidified by hydrochloric acid, the precipitate collected, and recrystallized from alcohol. A 92% yield of 2, 6-difluoro-4-hydroxybenzoic acid was obtained.

KOH 2.8 g (50 mmol) in 50 mL of distilled water was added to a slurry of 2, 6-difluoro-4-hydroxybenzoic acid (25 mmol) in ethanol (200 mL), and the mixture heated under reflux for 1 h. hexyl bromide (75 mmol) was added and the mixture was heated a further 12 h. KOH water solution (100 mL, 10%) was added and reflux continued for 2 h. After cooling, the mixture was acidified by hydrochloric acid and filtered. The crude product was recrystallized from ethanol giving a 70% yield of 6DFABA. IR, ν/cm^{-1} : 2530–3118 (acidic —OH), 1692 (C=O), 1575, 1450 (aromatic C=C), 1277 (C—O—Ar). ^1H NMR (400 MHz, CDCl_3): δ 0.90–1.81 (m, 11H, alkyl protons), δ 3.96–3.99 (d, 2H, $\text{—CH}_2\text{—O}$), δ 6.48–6.50 (d, 2H, Ar—H). ^{13}C NMR (100 MHz, CDCl_3): δ 13.57, 22.12, 25.10, 28.31, 31.02, 68.73, 98.66 (m, $^2J_{\text{CF}} = 26.3$ Hz), 101.73 (t, $^2J_{\text{CF}} = 14.9$ Hz),

163.53(t, $^3J_{\text{CF}} = 14.5$ Hz), 164.21(t, $^1J_{\text{CF}} = 257.5$ Hz), 166.97. Elemental analysis: calculated (found) for $\text{C}_{13}\text{H}_{16}\text{F}_2\text{O}_3$ C 60.46 (60.55), H 6.24 (6.21).

Synthesis of Hydrogen-Bonded Complexes (nFABA-BPy and nDFABA-BPy)

4, 4'-bipyridine (BPy) (0.001 mol) and 0.002 mol proton donors (nFABA and nDFABA) were dissolved in 5 mL of THF (tetrahydrofuran). The mixture was heated at 60°C and stirred for several minutes. Then, THF was removed under reduced pressure at room temperature. The resulting solid complexes were dried under vacuum at 60°C for 12 h to give the target complexes nFABA-BPy and nDFABA-BPy.

Results and Discussion

The intermolecular hydrogen bonding between the proton donors and acceptors was identified by IR spectra. Figure 3 shows the IR spectra of 6FABA, 6DFABA, 6FABA-BPy, and 6DFABA-BPy in the band range $4000\text{--}1600\text{ cm}^{-1}$.

The broad bands of 6FABA and 6DFABA in the range of $2500\text{--}3200\text{ cm}^{-1}$ suggested the strong interaction between the carboxyl of the proton donors. While in the spectra of 6FABA-BPy and 6DFABA-BPy, the disappearance of these broad bands and the appearance of the characteristic stretching of hydrogen bonds centered around 1500 and 1900 cm^{-1} indicated the formation of the hydrogen bonding between the carboxylic acid and BPy [6]. Furthermore, the characteristic stretching band of the carbonyl of 6FABA and 6DFABA was centered at 1684 and 1696 cm^{-1} , while in the corresponding complexes, they shifted to 1692 and 1709 cm^{-1} , which also suggested the formation of hydrogen bonds [18].

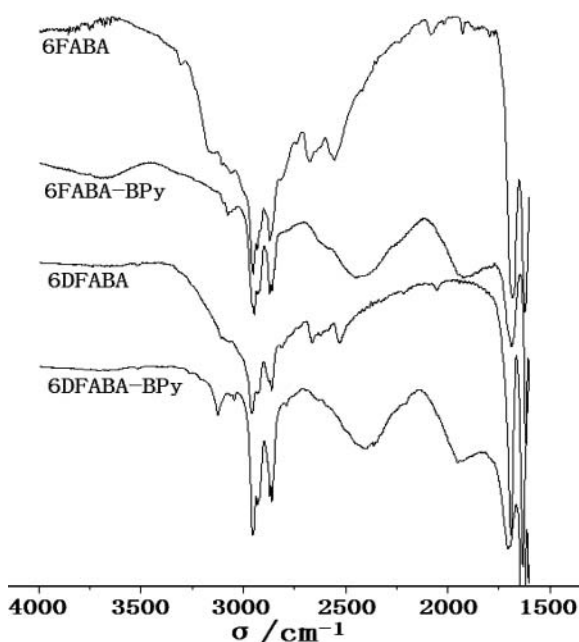


Figure 3. IR spectra of 6FABA, 6DFABA.

Table 1. Phase transition temperature and associated enthalpy changes of proton donors and acceptor

<i>n</i>	Phase transition temperature (°C) and enthalpy changes (J g ⁻¹ , in parentheses)*	
	nFABA	nDFABA
2	Cr $\xrightleftharpoons[183]{191(166.7)}$ I	Cr $\xrightleftharpoons[179]{188(24.6)}$ I
3	Cr $\xrightleftharpoons[119]{126(116.5)}$ I	Cr $\xrightleftharpoons[126]{137(31.7)}$ I
4	Cr $\xrightleftharpoons[99]{107(74.2)}$ N $\xrightleftharpoons[113]{115(7.5)}$ I	Cr $\xrightleftharpoons[109]{115(97.5)}$ I
5	Cr $\xrightleftharpoons[82]{109(114.2)}$ N $\xrightleftharpoons[116]{118(5.9)}$ I	Cr $\xrightleftharpoons[89]{100(103.7)}$ I
6	Cr $\xrightleftharpoons[103]{111(54.7)}$ N $\xrightleftharpoons[119]{122(6.6)}$ I	Cr $\xrightleftharpoons[93]{101(107.5)}$ I
BPy		
	Cr $\xrightleftharpoons[99]{113(63.8)}$ I	

*Cr: crystal; N: nematic; I: isotropic.

It is well-known that some 4-substituted benzoic acids exhibit mesomorphic properties due to the dimerization of carboxylic groups. So, in the present study, the thermal properties of the proton donors and acceptors were studied by POM and DSC and results were listed in Table 1. It could be seen from Table 1 that 2FABA and 3FABA showed no mesomorphic properties while 4FABA, 5FABA, and 6FABA exhibited a nematic phase and a tendency of increased thermal range and nematic-isotropic (N-I) transition temperature of mesophase. In series nDFABA, the two lateral fluorine atoms introduced into their mesogenic core caused a decrease of their slenderness ratio, which was considered an unfavorable factor for the formation and stability of their mesophase. So, unlike series nFABA, none of nDFABA studied in this paper are mesomorphic.

The liquid crystalline properties of the two series of fluorinated hydrogen-bonded complexes were studied by DSC, POM, and XRD. The phase variants, transition temperatures, and associated enthalpy of these complexes were listed in Table 2. And for more intuitively, the phase graphs of the two series of complexes were also provided in Fig. 4.

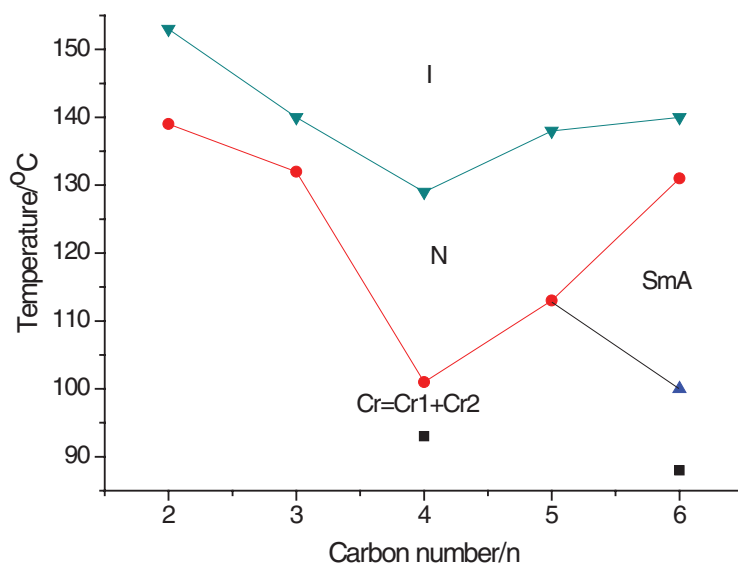
As can be seen from Table 2, the enthalpy of the N-I transition of the complex 6FABA-BPy is very larger than that of its smectic-nematic (SmA-N) transition and other N-I transitions in its series. This seemed a bit abnormal, so, we repeated the DSC measurement of the complex 6FABA-BPy, but the results showed no distinct difference with the data in the paper. A possible reason is that another phase transition with a very short mesomorphic range existed, which can not be differentiated by DSC, and the enthalpy value could be a sum of transition of this mesophase and transition of N-I.

Table 2. Phase transition temperature and associated enthalpy changes of nFABA-BPy and nDFABA-BPy

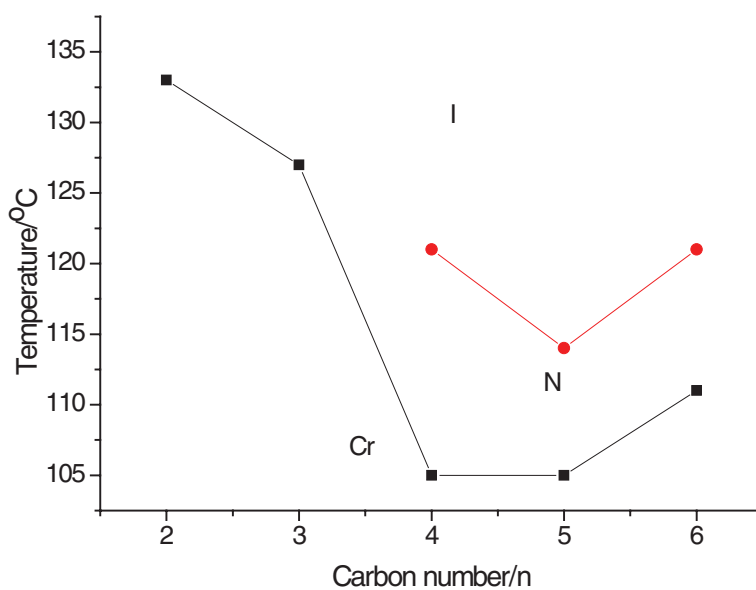
Complex	Phase transition temperature (°C) and enthalpy changes (J g ⁻¹ , in parentheses)*
6FABA-BPy	Cr1 $\xrightleftharpoons[88]{92(16.3)}$ Cr2 $\xrightleftharpoons[100]{105(25.7)}$ SmA $\xrightleftharpoons[131]{133(0.1)}$ N $\xrightleftharpoons[140]{143(8.6)}$ I
5FABA-BPy	Cr $\xrightleftharpoons[113]{120(39.3)}$ N $\xrightleftharpoons[138]{141(6.5)}$ I
4FABA-BPy	Cr1 $\xrightleftharpoons[93]{96(2.9)}$ Cr2 $\xrightleftharpoons[101]{109(17.7)}$ N $\xrightleftharpoons[129]{132(6.9)}$ I
3FABA-BPy	Cr $\xrightleftharpoons[132]{139(71.4)}$ N $\xrightleftharpoons[140]{143(3.7)}$ I
2FABA-BPy	Cr $\xrightleftharpoons[139]{164(116.6)}$ N $\xrightleftharpoons[153]{153}$ I
6DFABA-BPy	Cr $\xrightleftharpoons[111]{119(57.0)}$ N $\xrightleftharpoons[121]{125(3.9)}$ I
5DFABA-BPy	Cr $\xrightleftharpoons[105]{119(53.2)}$ N $\xrightleftharpoons[114]{114}$ I
4DFABA-BPy	Cr1 $\xrightleftharpoons[100(6.3)]{100(6.3)}$ Cr2 $\xrightleftharpoons[105]{123(56.1)}$ N $\xrightleftharpoons[121]{121}$ I
3DFABA-BPy	Cr1 $\xrightleftharpoons[96(2.9)]{96(2.9)}$ Cr2 $\xrightleftharpoons[127]{135(68.9)}$ I
2DFABA-BPy	Cr $\xrightleftharpoons[133]{156(93.8)}$ I

*Cr: crystal; Sm A: smectic A; N: nematic; I: isotropic.

It was obvious that the liquid crystalline properties of these complexes were very different from their precursor, which suggested that the hydrogen bonding were responsible for their mesophases. Table 2 also revealed that the number of fluorine atoms introduced into the complexes and the number of carbon atoms in alkoxy group have significant effect on the thermal stability of their mesophases. For series nFABA-BPy, in the higher homologue (number of carbon atoms in alkoxy group, $n = 6$) both nematic (Schlieren texture) and smectic A (Fan-shaped texture, and dark texture in vertically aligned sample) properties could be observed [Figs. 5(a), (b), and (e)]; in their lower homologues ($n = 2-5$), only one enantiotropic or monotropic mesophase (Schlieren texture) was observed [Fig. 5(c)]. While for series nDFABA-BPy, only 6DFABA-BPy exhibited enantiotropic nematic phase [Fig. 5(d)], and complexes 5DFABA-BPy and 4DFABA-BPy only exhibited monotropic nematic phase; as to 3DFABA-BPy and 2DFABA-BPy, no mesomorphic properties were observed. When compared nFABA with their corresponding analogs in series nDFABA, it could be found that the former provided a more favorable capacity for the formation and stabilization of the newcoming mesophase caused by hydrogen bonds than the latter.



(a)



(b)

Figure 4. Phase graphs of nFABA-BPy and nDFABA-BPy. (a) Phase graph of nFABA-BPy (on cooling cycle); (b) Phase graph of nDFABA-BPy (on cooling cycle).

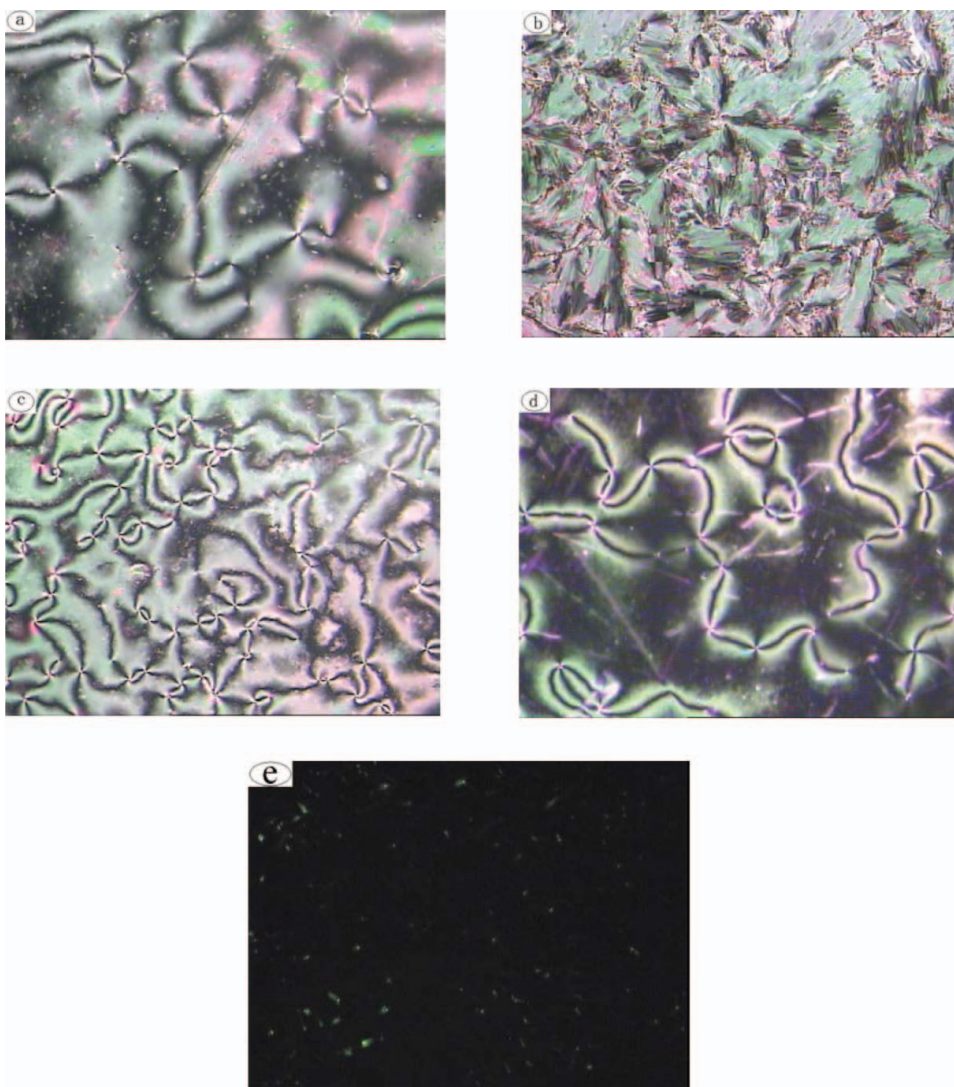


Figure 5. Optical textures of the hydrogen-bonded complexes. (a) Schlieren texture of 6FABA-BPy at 138.5°C ($\times 100$); (b) Fan-shaped texture of 6FABA-BPy at 129.8°C ($\times 200$); (c) Schlieren texture of 5FABA-BPy at 137.2°C ($\times 100$); (d) Schlieren texture of 6DFABA-BPy at 119°C ($\times 200$); (e) Dark texture of 6FABA-BPy at 127.5°C ($\times 400$).

As compared the two series with their nonfluorinated analogs, for example, the complex consisted of 4-butylbenzoic acid and BPy [19], it can be found that the number of phase variant and the thermal range of mesophase both decreased with the increase of fluorine atoms introduced into the complexes, which further confirmed that the introduction of lateral fluorine atoms went against the stability of mesophases. And when compared with their analogs that of same core structure but different kind of tail as reported in reference 17, it can be found that the tail also have effect on their mesomorphic properties. The ones

Table 3. XRD results of 6FABA

Compound	Temperature/°C	Phase	d/nm	L/nm
6FABA	126	SmA	39.3	42.7

have unsaturated tails possess a broader thermal range of mesophase, or more easily to form and stabilize a mesophase.

In these complexes with the same “alkoxy tail” and same proton acceptor, their slenderness ratio mainly lied on the width of the proton donors. With the data of bond lengths and bond angles of C—C, C=C, C—H, and C—F bonds provide by the software Chemoffice 2004, we can figure out the core width of the proton donors are 0.437 nm for 4-butoxybenzoic acid, 0.456 nm for 4FABA and 0.475 nm for 4DFABA. Obviously, the increased width of the proton donors decreased the slenderness ratio of the complexes, which is usually considered a disadvantageous factor to the formation of the mesophase [17].

The smectic phases of 6FABA-BPy were further studied by temperature-dependant XRD to confirm its Sm A natures. The XRD patterns contain a single sharp maximum at small angle, due to the reflection of X-rays on the smectic layers, and a diffuse and broad scattering peak at large angle, related to the liquid-like packing inside the layers. From Bragg’s law, the layer spacing d in the smectic structure could be calculated. The measured value of this parameter is listed in Table 3 together with the length L of the 6FABA-BPy molecule in their fully extended conformation, measured using Dreiding stereomodels.

It can be seen from Table 3 that the measured layer thickness d is slightly smaller than the calculated molecular length L , which confirms that the smectic phase has a structure of vertical molecules, which confirmed the smectic A phase [20].

Conclusion

Two series of superamolecular liquid crystals with laterally fluorinated species have been built through hydrogen bonding between the carboxyl group of fluorinated alkoxybenzoic acid and the pyridyl ring of 4, 4'-bipyridine. The thermal transition temperatures, mesomorphic properties, and mesophase texture of the complexes were characterized via DSC and POM. It was found that the introduction of lateral fluorine atoms had bad effect on the formation and thermal stability of the mesophase of the hydrogen-bonded complexes.

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